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(Article begins on next page)



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Simultaneous determination of passivator and antioxidant additives in insulating mineral oils by high performance liquid chromatography

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ABSTRACT

Insulating mineral oils frequently contain additives to improve their inherent characteristics, such as oxidation stability (antioxidants), electrostatic charging tendency and compatibility with other materials (passivators). Despite standard test methods are available for the detection of individual additives, none of them covers the simultaneous detection of additives of different kind. For the first time the simultaneous determination of antioxidants and passivators most frequently added to mineral insulating oils is provided. The compounds investigated included three inhibitors (N-phenyl-1-naphthylamine, 2,6-di-tert-butylphenol and 2,6-di-tert-butyl-p-cresol) and two passivators (benzotriazole and Irgamet 39). A solid phase extraction step, aimed at the reduction of matrix oil components was optimized. Due to the hydrophobic characteristics of the additives, a reversed-phase chromatographic separation was used and optimized. The method here developed was applied to the analysis of inhibited and passivated transformer oils, compared with Standard IEC60666 method, which requires the use of FT-IR spectrophotometry (measurement of the adsorption corresponding to the stretching $\nu(\text{OH})$ of the phenol group at 3650 cm^{-1}), and finally applied inside an ASTM Proficiency Testing Program. In a unique analysis, the method provides a tool to assess chemical composition and concentration of oil additivation, and it allows discrimination among phenolic inhibitors.

KEYWORDS: SPE-HPLC; mineral oil; passivators; inhibitors; antioxidants; oil monitoring

Abbreviations: **BTA:** benzotriazole; **Irgamet 39:** mixture of N,N-bis(2-ethylexyl)-4-methyl-1H-benzotriazol-1-methylamine, and N,N-bis(2-ethylexyl)-5-methyl-1H-benzotriazol-1-methylamine; **NPN:** N-phenyl-1-naphthylamine; **DBP:** 2,6-di-tert-butyl-phenol; **DBPC:** 2,6-di-tert-butyl-p-cresol

INTRODUCTION

The quality of mineral insulating oils in power transformers can change as a result of oil ageing and/or due to other chemical reactions that may compromise the insulating properties of the oil itself. Long term performance of mineral insulating oil can be improved by using specific additives that retard the deterioration processes. Addition of metal passivators as Irgamet 39 is the most widely applied mitigating technique for corrosive sulphur. Irgamet 39 is a mixture of 2 isomers: N,N-bis(2-ethylexyl)-4-methyl-1H-benzotriazol-1-methylamine and N,N-bis(2-ethylexyl)-5-methyl-1H-benzotriazol-1-methylamine (Figure 1). Other passivators, such as benzotriazole (BTA, Figure 1) are used to reduce the electrostatic charging tendency of the oil.

To prevent oxidation, antioxidants (or inhibitors) are added to the oil. Inhibitors commonly added include 2,6-di-tert-butyl-p-cresol (DBPC), 2,6-di-tert-butylphenol (DBP) and N-phenyl-1-naphthylamine (NPN), (Figure 1).

Antioxidants are usually added up to 0.08% (trace inhibited oils) and 0.08 to 0.4% (inhibited oils),^[1] while passivators are added in the range 0.01-0.02%.^[2] If the concentration of antioxidant depletes below 40-60% of its initial concentration, maintenance guides suggest to restore it^[3]. Due to thermal or chemical degradation, passivators also may decay with time, and are often restored when their concentration becomes insufficient to protect copper from corrosion.

The monitoring of the content of antioxidant and passivator in insulating oil is an important aspect of transformer management since it can extend the service life of the oil and slow down the transformer ageing process.

So far, the determination of antioxidants and passivators requires different techniques. According to the International Electrotechnical Commission (IEC), phenolic antioxidants can be determined by one of the following approaches:^[4]

(i): FT-IR spectrophotometry. This method is recommended for the determination of DBPC and DBP, but does not discriminate between them. It can be directly used with new oils, but is less satisfactory for used oils since oxidation by-products interfere with the determination;

(ii): GC-MS. This method is applicable for the determination of DBPC and DBP also for mineral oils for which IR methods suffer from interferences;

Two additional standard methods, ASTM D2668 ^[5] and ASTM D4768 ^[6] recently re-approved, allow the determination of DBP and DBPC in insulating oils by IR and GC, respectively.

As far as HPLC is concerned, Lamarre and coworkers showed the challenge of determining DBPC^[7,8] and polar oxidation products^[9] in insulating oils. Alternative methods, such as differential pulse voltammetry,^[10] micellar electrokinetic capillary chromatography,^[11] have also been proposed for DBPC determination.

As regards the extraction of additives, different approaches are required for the determination of antioxidants and passivators and few research studies have been aimed at the development of a unique sample extraction technique. Although Jaber et al.^[12] recently proposed a liquid-liquid extraction method for the simultaneous extraction of BTA, DBPC and DBDS (dibenzyl disulfide), three different analytical methods (GC-FID, GC-ECD, HPLC) were required for the determination of the three species.

The possibility to assess composition and concentration of oil additivation by a single method is a demanding task and to the best of our knowledge, such an approach has not yet been developed or investigated.

The aim of this study was the optimization of a solid phase extraction (SPE)-HPLC method for the simultaneous determination of passivators and antioxidants. For this purpose, two triazolic passivators (BTA, Irgamet 39) and three antioxidants (NPN, DBP and DBPC) frequently added by manufacturers were selected for this study. The method developed was successfully applied to the determination of additives in insulating oils of different types sampled from in-service power transformers.

For the first time a unique method is provided for the determination of these five additives in a single chromatographic run.

EXPERIMENTAL

Chemicals and Material

BTA (>98%), DBPC (>99%), DBP (>98%) were from Fluka (Milan, Italy). Irgamet 39 was from Ciba-Geigy (Lumar Italia, Milan, Italy), NPN (98%) was from Acros Organics (Thermo Fisher, Milan Italy); pentane >99%. Methanol, acetonitrile and water were HPLC gradient grade (Panreac, Novachimica, Cinisello Balsamo, Milan, Italy).

Oil samples: The following oils samples were used throughout this work.

- *ITE 360 (Agip, Milan Italy)*, unused: insulating oil not containing additives according to oil's datasheet.

- *In service transformer oils (#1-#6)*. Six oils sampled from operating transformers (installed in Italian thermal and aeolian power plants and in interconnected transmission grids of Middle East). None of them was inhibited or had additives of the family of passivators and metal deactivators.

- *Hyvolt II (Ergon, Mississippi, USA)*, was an unused commercial oil inhibited with DBPC.

- *In service transformer oil A* was sampled from an in service steel plant transformer (France).
- *Proficiency test sample* was provided inside the ASTM Committee D-27 Proficiency Testing Program (ASTM PTP IFQ 1203).

Instrumentation

For chromatographic analysis, a HP 1100 Chemstation (Agilent, Milan, Italy) equipped with autoinjector and with a G1315B Agilent diode array detector was used. The column was 201SP C18 end-capped (250x4.6mm) 5 μ m, 90 Å (Grace, Deerfield, IL, USA). The eluent flow rate was 1 mL \cdot min⁻¹ and the injection volume was 20 μ L. Detection wavelengths were 265 nm for BTA, Irgamet 39 and NPN and 275 nm for DBP and DBPC.

For FT-IR measurements, a 330 Model Nicolet Avatar (Thermo Electron, Waltham, USA), with KBr windows with 0.54 mm optical path was used.

Sample preparation and SPE

For chromatographic optimization, additives (50 mg \cdot kg⁻¹) were prepared in eluent. For solid-phase extraction, 3 mL, 500 mg silica cartridges (Sep-Pak Plus, Waters, 318 m² \cdot g⁻¹, particle size 79.7 μ m) previously activated with 5 mL pentane were used. The extraction procedure, as optimized, was the following. Aliquots of 0.5 g oil in 2.5 mL pentane were loaded onto the SPE cartridge. The cartridge was dried under vacuum (10 min) and the additives were eluted with 5 mL 40:60 (% v/v) H₂O:CH₃CN.

SPE recoveries were evaluated in triplicate in matrix oil *ITE 360* spiked with 22 mg \cdot kg⁻¹ (0.0022 %) BTA, 51 mg \cdot kg⁻¹ (0.0051 %) Irgamet 39, 107 mg \cdot kg⁻¹ (0.0107 %) NPN, 552 mg \cdot kg⁻¹

(0.0552 %) DBP, 557 mg·kg⁻¹ (0.0557 %) DBPC. These concentrations are representative of depleted passivated oils and trace inhibited oils. A blank (*ITE 360*) was extracted in parallel.

RESULTS AND DISCUSSION

Optimization of chromatographic separation

The separation of the five additives was optimized comparing the performance of CH₃OH and CH₃CN as organic modifiers employed for their reversed phase-HPLC analysis. With both organic solvents, several mobile phase compositions for isocratic elution (ten levels, ranging from 0 to 100%) and different gradient profiles were tested to obtain the complete resolution of the five additives.

Whatever mobile phase composition and gradient profile were used, the retention order of the investigated additives was the following: BTA<Irgamet 39<NPN<DBP<DBPC, with obvious differences in resolution and peak shape. As shown in Figure 1, benzotriazole is expected to be the less hydrophobic compound among those investigated and, indeed, was the less retained. The hydrophobicity of Irgamet 39 in respect to BTA is expected to be enhanced by the presence of the methyl group (position 4 or 5 according to the isomer) and of the ramified alkyllic substituent on the same benzotriazolic structure, leading to stronger retention, as it was experimentally observed. Less evident appears to be the relationship between the chemical structure and the chromatographic retention of NPN and DBP, eluting after the Irgamet 39 isomers. NPN, which contains one naphthalenic structure and a benzene ring as aminic substituents, elutes before DBP, which is a phenol containing two tert-butyl groups. This compounds elutes earlier than DBPC whose hydrophobicity is expected to be enhanced by the addition of a -CH₃ group on the same structure.

Acetonitrile was preferred over methanol because it improved the separation of Irgamet 39 isomers and the gradient elution mode was necessary in order to separating DBP and DBPC in reasonable analysis times and to avoid coelution of BTA and Irgamet 39. Just as an example, the isocratic elution mode with 50:50 CH₃CN:H₂O (% v/v) provided the following retention times (t_R): 3.5 min (BTA), 4.2 min (Irgamet 39), 60.5 min (NPN), 87.3 min (DBP) and 113.1 min (DBPC); while 100% CH₃CN provided t_R : 3.0 min (BTA), 3.4 min (Irgamet 39), 4.1 min (NPN), 4.4 min (DBP) and 4.6 min (DBPC). Among the compositions tested, the gradient elution that provided the best results in terms of selectivity and resolution among species was: $t=0-10$ min 30:70 CH₃CN:H₂O (% v/v), $t=10-11$ min from 30:70 CH₃CN:H₂O (% v/v) to 80:20 CH₃CN:H₂O (% v/v), $t=11-20$ 80:20 CH₃CN:H₂O (% v/v), $t=20-21$ from 80:20 CH₃CN:H₂O (% v/v) to 100 CH₃CN. The optimized gradient includes a step of column washing after the elution of DBPC (about 23 min). A typical chromatogram is shown in Figure 2.

Sample extraction by SPE

The method of sample extraction by SPE was optimized using the *ITE 360* oil which was spiked with the five compounds under investigation. The experiments were performed in triplicate and the influence of dilution prior to sample loading onto the SPE cartridge and composition of the mobile phase for its elution were investigated. An aliquot of 0.5 g oil was diluted in pentane and loaded onto the silica cartridge. A silica based cartridge was chosen in order to remove the oil matrix and to retain the additives. The cartridge was dried under vacuum (10 min) and subsequently the retained additives were eluted with 5 mL of an aqueous:organic solvent mixture before HPLC analysis (see Section *Effect of the elution phase*).

Effect of dilution

For pentane volume higher than 2.5 mL (dilution ratios higher than 1:5, w/v), it was not possible to extract DBP and DBPC from the oil. The FT-IR analysis on the oil solution after loading onto the cartridge, revealed the presence of peaks at approximately 3650 cm^{-1} , characteristics of the (O-H) stretching frequency of hindered phenols. According to this result, a rinsing step of the cartridge after sample loading was not included in the extraction procedure. For further optimization, a 1:5 (w/v) dilution ratio was used.

Effect of the elution phase

To elute the retained compounds, the following mixtures of different polarities were tested: a) 100% H_2O ; b) 60:40 (% v/v) $\text{H}_2\text{O}:\text{CH}_3\text{OH}$; c) 40:60 (% v/v) $\text{H}_2\text{O}:\text{CH}_3\text{OH}$; d) 40:60 (% v/v) $\text{H}_2\text{O}:\text{CH}_3\text{CN}$; e) 100% CH_3OH ; f) 100% CH_3CN .

BTA, Irgamet 39 and NPN were recovered in reasonable amount with all the eluting phases, whereas the recovery of DBP and DBPC was significantly affected by the composition of the used eluent. Although DBP and DBPC were eluted by eluents c,d,e,f, eluent d provided recovery of additives with minor oil matrix elution.

Recoveries

The optimized extraction conditions were the following: 0.5 g oil in 2.5 mL pentane were loaded onto the SPE cartridge. The cartridge was then dried under vacuum for 10 min; and the additives were eluted with 5 mL 40:60 (% v/v) $\text{H}_2\text{O}:\text{CH}_3\text{CN}$.

The recovery yields obtained for additives in unused oil matrix (*ITE 360*) were: BTA: $76.7\pm1.6\%$; Irgamet 39: $84.9\pm2.6\%$; NPN: $85.6\pm4.8\%$; DBP: $51.2\pm3.9\%$ and DBPC: $15.2\pm2.4\%$.

As an example, a chromatogram obtained after SPE-HPLC analysis for spiked *ITE360* oil is shown in figure 3.

Recovery yields were verified through spike-addition recovery tests on six *in service transformer oils* (#1-#6). Oils were spiked with known concentrations of the five additives (250 mg·kg⁻¹ BTA and Irgamet 39, 490 mg·kg⁻¹ NPN, DBP and DBPC) and extracted according to the optimized procedure. Since the mean recoveries were BTA: 80.3±4.4%; Irgamet 39: 87.2±4.2%; NPN: 83.2±3.6%; DBP: 53.0±2.4% and DBPC: 14.7±1.9% (n=6), the quantification is not biased by the different matrix composition of the oils (i.e. by ageing).

Matrix matched calibration

Mixtures of *ITE360* oil were spiked with the five additives at different concentration levels and extracted by SPE. The extract was analysed by the optimized gradient HPLC method and peak areas were used to obtain matrix-matched calibration curves. Five concentration levels were chosen in order to include, for both passivators and antioxidants, the concentrations actually added in commercial oils. Concentrations ranged from 10-100 mg·kg⁻¹ (0.001-0.01 %) for BTA, 20-500 mg·kg⁻¹ (0.002-0.05 %) for Irgamet 39, 50-4000 mg·kg⁻¹ (0.005-0.4 %) for NPN, 300-4000 mg·kg⁻¹ (0.03-0.4%) for DBP and DBPC. The following equations were obtained: BTA: $y=3.068x-5.866$ ($r^2=0.9986$); Irgamet39: $y=0.973x+1.114$ ($r^2=0.9999$); NPN: $y=3.265x-135.48$ ($r^2=0.9915$); DBP: $y=0.383x+222.25$ ($r^2=0.9924$); DBPC: $y=0.3369x-13.848$ ($r^2=0.9915$).

Oil analyses

Unused *Hyvolt II* oil (inhibited by manufacturer with DBPC) and *in service transformer oil A* were analysed by the developed method. Twenty repeated extractions and HPLC analysis were

performed for each oil sample. Concentrations were obtained by the matrix-matched calibration graphs described above. As regards *Hyvolt II* oil, the DBPC content was $3114 \pm 470 \text{ mg}\cdot\text{kg}^{-1}$ (concentration declared by manufacturer: $<3000 \text{ mg/kg}$). A standard addition method was also applied (four DBPC additions in *Hyvolt II*, ranging from 1240 to $4160 \text{ mg}\cdot\text{kg}^{-1}$, extracted by SPE and analysed by HPLC), finding a concentration value of $3290 \text{ mg}\cdot\text{kg}^{-1}$ ($r^2=0.9943$). As regards the unknown sample labelled *in service transformer oil A*, Irgamet 39 was the only compound present ($126.4 \pm 4.1 \text{ mg}\cdot\text{kg}^{-1}$).

The concentrations found for the two oil samples were compared with those obtained by applying the Standard IEC60666 method^[4] (Table 1), that is HPLC for Irgamet 39 and FT-IR for DBPC. The values measured by the Standard method for Irgamet 39 ($120 \text{ mg}\cdot\text{kg}^{-1}$) and for DBPC ($3470 \text{ mg}\cdot\text{kg}^{-1}$) well compare with those obtained by the method optimized. The differences between the values obtained by the method here developed and those measured by the Standard method ($120 \text{ mg}\cdot\text{kg}^{-1}$ for Irgamet 39 and $3470 \text{ mg}\cdot\text{kg}^{-1}$ for DBPC), divided by the target values (assumed to be the ones measured by IEC 60666), are respectively: 0,053 for Irgamet39 and 0,052 for DBDC; both values are included in the reproducibility values described in the Standard method (8% for Irgamet39 and 45% for DBPC).

The SPE-HPLC method was finally applied inside a Proficiency Testing Program (ASTM PTP IFQ 1203), prescribing a FT-IR method^[4] for the analysis of an oil sample containing DBPC (Table 1). The acceptability of the results is assessed according to the absolute values of z-scores ($|z| \leq 2$ acceptable result; $2 < |z| < 3$ doubtful result; $|z| \geq 3$ unacceptable result). Since $|z|= 1.95$ (for assigned, measured values and target standard deviation see Table 1), the result obtained by the proposed method is included within the acceptable result range.

CONCLUSIONS

In this work, for the first time a SPE-HPLC method was optimized and validated for the simultaneous analysis of five common additives in insulating oils usually determined by different chromatographic techniques (GC and LC) or by spectrophotometric approaches (FT-IR).

This approach provides a powerful screening tool to assess the composition and concentration of oil additivation (presence of inhibitors and/or passivators) when this is unknown (that is in the majority of the cases for transformers in service). In addition, the developed method allows to understand if an oil can be classified as inhibited and moreover, differently from FT-IR method recommended by IEC,^[4] it allows to discriminate among phenolic compounds.

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Figure Captions

Figure 1. Chemical structure of oil additives.

Figure 2. Optimized gradient elution for the simultaneous elution of passivators (BTA, Irgamet 39) and antioxidants (NPN, DBP, DBPC). Additive concentrations: 50 mg·kg⁻¹ (0.005 %) each.

Figure 3. SPE and HPLC separation of additives in commercial oil matrix (*ITE 360*, Agip) according to the protocol optimized. Sample: *ITE 360* spiked with 0.006 % BTA, 0.02% Irgamet 39, 0.15% NPN, 0.15% DBP, 0.15% DBPC.

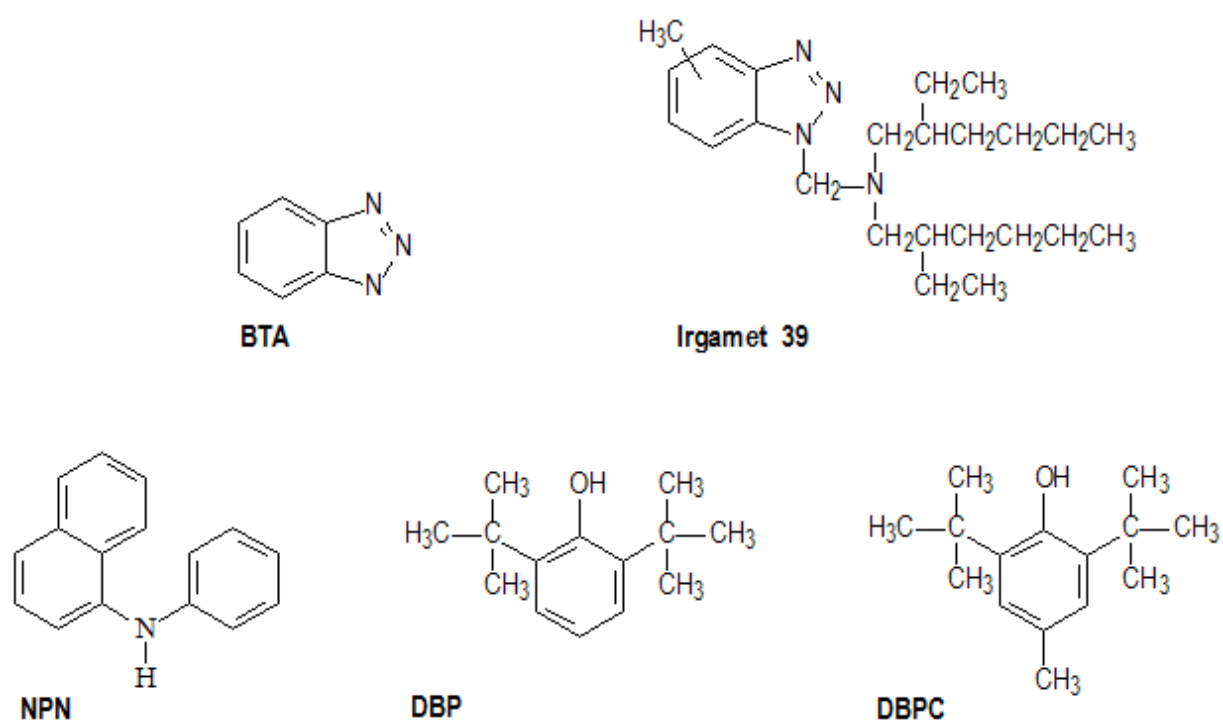


Figure 1.

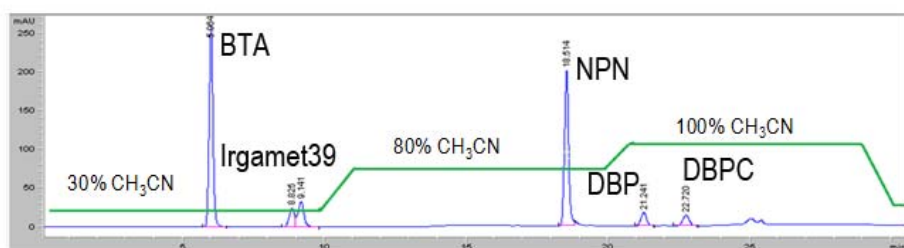


Figure 2.

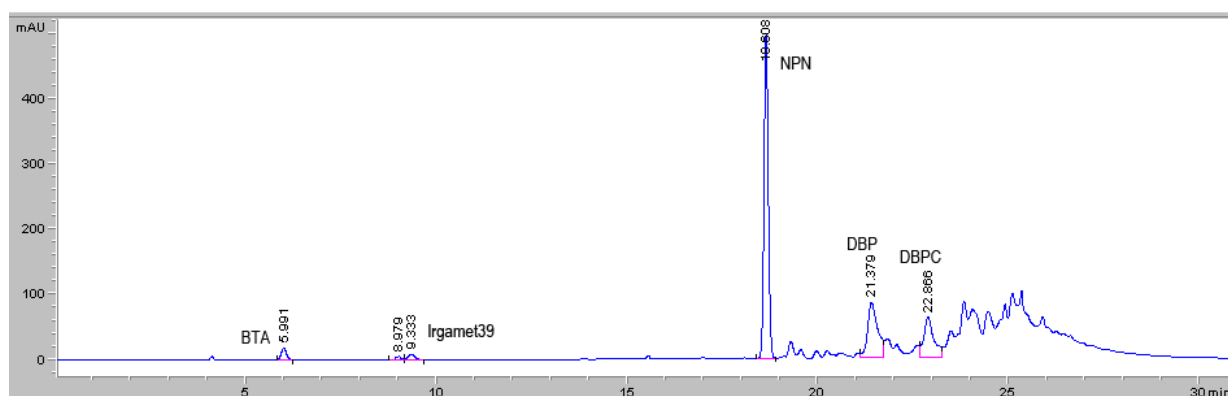


Figure 3.

Table 1. Analysis of commercial and blind oils by the method developed and comparison with Standard IEC60666.

Oil sample	Additive contained	Concentration (mg·kg ⁻¹) This method	Concentration (mg·kg ⁻¹) Standard IEC60666
<i>In service transformer oil A</i>	Irgamet 39	126±4, n=20	120
<i>Hyvolt II^{a)}</i>	DBPC	3114 ± 470, n=20	3470 ^{b)}
<i>Proficiency test sample^{c)}</i>	DBPC	798	1140

a) Concentration determined by standard addition method after SPE: 3290 mg·kg⁻¹.

b) Concentration declared by manufacturer: <3000 mg·kg⁻¹.

c) $|z| = \left| \frac{x_{mj} - x_M}{\sigma_p} \right|$; x_{mj} = value measured with the SPE-HPLC procedure; x_M = target value= 1090

mg·kg⁻¹; σ_p = target standard deviation= 150 mg·kg⁻¹.